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# Determination of dimethyl selenide and dimethyl sulphide compounds causing off-flavours in bottled mineral waters

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## Abstract

Sales of bottled drinking water have shown a large growth during the last two decades due to the general belief that this kind of water is healthier, its flavour is better and its consumption risk is lower than that of tap water. Due to the previous points, consumers are more demanding with bottled mineral water, especially when dealing with its organoleptic properties, like taste and odour. This work studies the compounds that can generate obnoxious smells, and that consumers have described like swampy, rotten eggs, sulphurous, cooked vegetable or cabbage. Closed loop stripping analysis (CLSA) has been used as a pre-concentration method for the analysis of off-flavour compounds in water followed by identification and quantification by means of GC-MS. Several bottled water with the aforementioned smells showed the presence of volatile dimethyl selenides and dimethyl sulphides, whose concentrations ranged, respectively, from 4 to 20 ng/L and from 1 to 63 ng/L. The low odour threshold concentrations (OTCs) of both organic selenide and sulphide derivatives prove that several objectionable odours in bottled waters arise from them. Microbial loads inherent to water sources, along with some critical conditions in water processing, could contribute to the formation of these compounds. There are few studies about volatile organic compounds in bottled drinking water and, at the best of our knowledge, this is the first study reporting the presence of dimethyl selenides and dimethyl sulphides causing odour problems in bottled waters.

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**Keywords:** Dimethyl selenide; Dimethyl sulphide; Bottled drinking water; Off-flavour; CLSA

## 1 Introduction

Organoleptic properties of water are some of the most influential factors when choosing a bottled water brand, and among them, flavour may be considered the most important one (Doria et al., 2009; Marcussen et al., 2013). Consumption of bottled still water has been increasing around the world for the last twenty years. In Europe, consumers purchase and drink more than 52 billion litres of bottled water every year, of which 84% is natural mineral water, and the average consumption per inhabitant is 103 L, being in Spain 113 L (EFBW, 2015). Although the quality of tap water is getting better because it is controlled by rigorous standards and frequently analysed (Olson, 1999), most consumers believe that bottled water has better quality, health benefits and flavour than tap water (Doria, 2006; Massoud et al., 2013; Ward et al., 2009).

The legislation regulating bottled water in Spain is set out in Royal Decree 1798/2010 (BOE, 2010) adapting European directives 2009/54/EC (EP, 2009). Under this decree, mineral water is defined as water from underground sources, and microbiologically healthy. No treatment able to change the water natural composition can be applied to a mineral water. The only allowed processes are filtration, oxygenation, settling and treatment with ozone-rich air.

Bottled water is not a sterile food product because it is not free of bacteria (Semerjian, 2011). Bottled water contains a characteristic bacterial flora and microorganisms coming from the natural mineral water itself or due to contamination during the bottling stage and time out on the market (Rosenberg, 2003; Tsai and Yu, 1997; Vantarakis et al., 2013; Warburton et al., 1998). Raw water source, treatment of water, bottling process, wet storage area, poor quality of bottle and packaging may be considered as potential contributors of organic pollutants and, consequently, as precursors of off-flavours.

In bottled water, bacteria could be indigenous from the natural source of water (Rosenberg, 2003) or could be introduced during the collecting, processing and bottling stages (Warburton, 2000). Despite the legislation on microorganisms

in bottled water, it has been reported that after storage, they may multiply and exceed  $10^4$  cfu/mL (Warburton et al., 1998). It has also been demonstrated that the storage temperature of bottled water influences the multiplication rate and survival of microorganisms (Bischofberger et al., 1990; Herath et al., 2012).

Most studies about organic compounds found in bottled mineral waters are about the influence of the packaging material. The foregoing may be due to a migration caused by storage at high temperatures (Al-Mudhaf et al., 2009; Bach et al., 2013, 2012; Nawrocki et al., 2002; Page et al., 1993) or poor results of manufacturing. Other organic contaminants have been considered, like pesticides (Diaz et al., 2009; Gibbons and Laha, 1999) or perfluoro derivatives (Ericson et al., 2008). Another source of contamination may be the water treatments which, joined to the bottle cleaning, can generate compounds like trihalomethanes (Ahmad and Bajahlan, 2009; Al-Mudhaf et al., 2009; Gibbons and Laha, 1999; Ikem, 2010; Leivadara et al., 2008; Liu and Mou, 2003) or haloacetic acids (Leivadara et al., 2008; Liu and Mou, 2003).

Several methods have been described in the literature for the isolation and/or concentration of volatile organic compounds from water samples aimed to analyse organic traces. Techniques like purge and trap (P&T), simultaneous distillation extraction (SDE, aka Likens-Nickerson method), liquid–liquid extraction (LLE), solid-phase microextraction (SPME), closed loop stripping analysis (CLSA) and stir-bar sorptive analysis (SBSA), have been widely applied (Chary and Fernandez-Alba, 2012). Among the above methods, CLSA, according to the method first described by Grob (Grob, 1973) and Krasner and co-workers (Hwang et al., 1984; Krasner et al., 1983), is one of the most powerful tools to isolate the compounds responsible for taste and odour in water. Gas-chromatography coupled to mass spectrometry (GC–MS) technique allows the identification and quantification of a large number of VOCs within one single run with limits of detection at ng/L.

When some off-flavour is detected by consumers they will likely reject this water because they will consider that drinking it can be hazardous. Although this odour/taste may influence on consumers, it cannot be correlated with any health risk.

Dealing with complaints about different types of odours found in bottled waters by consumers, scores of samples have been analysed. Many claims were based on samples with undefined flavours similar to rotten eggs, sulphurous, cooked vegetable, swampy and/or cabbage, whose characteristics were different from other claims and relatively easy to describe. The CLSA extraction method has been widely applied to isolate many volatile organic compounds responsible for taste and odour episodes in water contributing to water smell. The extractions carried out with this method have allowed to detect compounds like aldehydes, ketones, trihalomethanes, pirazynes, methylisoborneol, geosmine, etc (Gun et al., 2000; Malleret et al., 2001; Ventura et al., 1997). However, no compound justifies the intense aforementioned smells described by the consumers.

The aim of this work is the study of the volatile organic compounds responsible for generating these objectionable odours in bottled mineral water. CLSA was applied as extraction method followed by GC–MS as analytical technique used to quantify and identify the target compounds present in bottled water.

## 2 Materials and methods

### 2.1 Bottled mineral water samples

The samples provided by bottled mineral water companies—all of them subject of complain about their off-flavour—were stored at 4 °C until they were analysed within 48 h. The bottles were polyethylene terephthalate (PET) containers with polyethylene (PE) caps. The volumes of the bottles were 0.33, 0.5 and 1.5 L.

### 2.2 Reagents and chemicals

Standards of dimethyl disulphide (DMDS), dimethyl trisulphide (DMTS), dimethyl tetrasulphide (DMTES) dimethyl diselenide (DMDS<sub>2</sub>) and 1-chloroalkanes (C<sub>5</sub>, C<sub>6</sub>, C<sub>8</sub>, C<sub>10</sub>, (OK)<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub> and C<sub>18</sub>) were purchased from Sigma–Aldrich (St. Louis, Missouri, USA). Stock solutions of 1-chloroalkanes were prepared for controlling CLSA recuperations at concentrations of 40 ng/L and 200 ng/L. Different solutions of DMDS, DMTS and DMDS<sub>2</sub> were prepared for quantification and DMTES for identification. Acetone was purchased from Burdick & Jackson (Seelze, Germany) and CS<sub>2</sub> from Fluka (Buchs, Switzerland).

### 2.3 Sample extraction: closed loop stripping analysis (CLSA)

The extraction and concentration of volatile organic compounds present in bottled waters were carried out using a commercial CLSA 9000 apparatus (Brechtbüler, Switzerland) following the method described in Standard Methods for the Examination of Water & Waste Water (Eaton et al., 1999), slightly modified. First, 950 mL of bottled water samples were spiked with 10 µL of 1-chloroalkanes (C<sub>5</sub>, C<sub>6</sub>, C<sub>10</sub>, C<sub>12</sub>, C<sub>16</sub> and C<sub>18</sub>) in acetone as internal standards at 40 ng/L. Then, VOCs and standards were stripped by air at a flow rate of 4.2 L/min for 1 h. The recirculating air was passed through the water sample held at 45 °C in the water bath, and then, the gas stream leaving the sample was heated 15 °C above the water bath temperature in order to prevent water condensation. Then, VOCs are retained onto 1.5 mg of activated charcoal trap. Finally, the organic compounds adsorbed by the activated charcoal were eluted from the carbon trap, previously spiked with 2 µL of 1-chloroalkanes (C<sub>8</sub> and C<sub>14</sub>) at 200 ng/L to check the extraction procedure, with 16 µL of CS<sub>2</sub> in two consecutive extractions (2 × 8 µL) and finally 2 µL of CS<sub>2</sub> were added to reach a final volume of 20 µL.

## 2.4 GC MS Analysis conditions

Aliquots of the eluate from the activated charcoal after applying CLSA extraction method were analysed by GC–MS (Trace MS Plus, Thermo Finnigan, San Jose, California). The GC system was equipped with a DB-5 column (J&W) (60 m × 0.25 mm × 0.25 µm). 1 µL of aliquot was injected by cold on column injection mode. Helium was used as carrier gas (1 mL/min). Temperature program ranged from 35 °C to 280 °C in the following way: 35 °C held for 5 min, increasing at 5 °C min<sup>-1</sup> up to 280 °C, held for 10 min. A 5 min solvent delay was programmed when the samples were injected. Spectra were obtained on electron ionization at 70 eV. Data were processed using Excalibur software and Wiley 6.1 (NY, USA) and Nist 05 libraries were used. The samples were analysed both in scan mode (from *m/z* 35 to 350, 0.5 s/scan) to identify their compounds and in selected ion monitoring (SIM) for their quantification. Compounds were identified by comparing the retention times and mass spectra of standards indicated before.

## 2.5 Quantitative measurements

In order to evaluate the performance of the method for the analysis of water samples, linearity, instrumental detection limits (IDLs), instrumental quantification limits (IQLs), repeatability, reproducibility and recoveries in bottled water were calculated and they were determined by cold on-column injection. These quantification and detection parameters for quantification are shown in Table 1.

Table 1 Correlation coefficients, detection limits and recoveries of DMDS, DMTS and DMDSe.

Compound	DMDS	DMTS	DMDSe
Linear range (ng/L)	1–23	1–24	1–28
Correlation coefficient R <sup>2</sup>	0.9997	0.9994	0.9993
IDL (ng/L)	0.036	0.055	0.086
IQL (ng/L)	0.103	0.18	0.3
Repeatability (% RSD)			
1 ng/L	3.92	1.33	3.42
2 ng/L	1.43	2.11	1.98
7 ng/L	3.96	3.16	3.18
10 ng/L	3.95	1.22	3.98
Reproducibility (% RSD)			
1 ng/L	4.6	9.56	9.89
2 ng/L	7.14	5.63	6.18
7 ng/L	5.7	6.60	7.29
10 ng/L	5.62	9.46	5.75
Recovery (%)			
10 ng/L	51	98	38
20 ng/L	62	98	41

The linearity range of the method was evaluated by plotting the calibration curves of the ratio between the area of the analyte and the closest internal standard (1-chloroalkane C<sub>6</sub>) versus the ratio between the concentrations of the analyte and the same internal standard. To determine the linearity, seven different concentrations were analysed in four replicates over a range of concentrations in water from 1 to 23 ng/L for DMDS, from 1 to 24 ng/L for DMTS and from 1 to 28 ng/L for DMDSe. The correlation coefficients obtained for each compound of the calibration curves were then calculated from the previous data. Compound peak responses were integrated using Sacitzky-Golay smoothing.

The IDLs and IQLs were calculated as the average signal of the lowest level of standard solution for each compound (n = 3) plus three- and tenfold the standard deviation, respectively. The units of IDL and IQL results were finally converted from ng/L to pg injected on GC–MS column according to 1 µL injection volume.

The repeatability was determined by injecting four concentration levels of each analyte five times on the same day and reproducibility was calculated by injecting the same concentration levels on five different days.

To determine the recoveries of DMS, DMTS and DMDSe, the standard solutions were spiked at 10 ng/L and 40 ng/L into bottled water (n = 3) and then CLSA extractions were carried out following the same procedure used for original samples. To calculate the recoveries in all samples, the recoveries of the internal standards (1-chloroalkanes C<sub>5</sub>, C<sub>6</sub>, C<sub>10</sub>, C<sub>12</sub>, C<sub>16</sub> and C<sub>18</sub>), added before extraction, were calculated relative to 1-chloroalkanes C<sub>8</sub> and C<sub>14</sub>, added after extraction.

Due to DMTES had been only detected in one sample, the quantification and detection parameters applied for it were the ones obtained from DMTS. Relative response factor (RRF) for DMTES was estimated by injecting standard concentrations of the analytes and comparing the resulting peak areas with the peak area of the closest chloroalkane.

Each sample batch was always complemented with its corresponding extraction from a blank sample for evaluating the repeatability of the method. Extractions of blank samples were injected between extractions from bottled waters. Three additional blanks were injected after the most concentrated internal calibration standard to check cross talking between injections.

### 3 Results and discussion

#### 3.1 Identification of the off-flavour compounds in commercial bottled waters

30 bottled water samples presented the swampy, rotten eggs, sulphurous, cooked vegetable and/or cabbage off-flavour and, after analysis, 23 of them contained methyl derivatives of sulphur whose odour threshold concentration (OTC) is very low, and derivatives of selenium whose OTC was unknown. From that moment, analytical efforts were aimed at detecting these compounds.

The explanation of the presence of these compounds may be found in the composition of the soil in contact with underground waters. The presence of sulphur and selenium may trigger some chemical reactions and generate their methyl derivatives identified in the samples. These reactions have been studied and published by several authors such as those reviewed in 3.1.1 and 3.1.2.

And owing to the low concentrations of the compounds which have been detected, CLSA was able to extract them in order to analyse and quantify the samples. The conditions in scan mode (from *m/z* 35 to 350, 0.5 s/scan) permitted to obtain a clear mass spectrum and well defined peaks (Figs. 1 and 2).

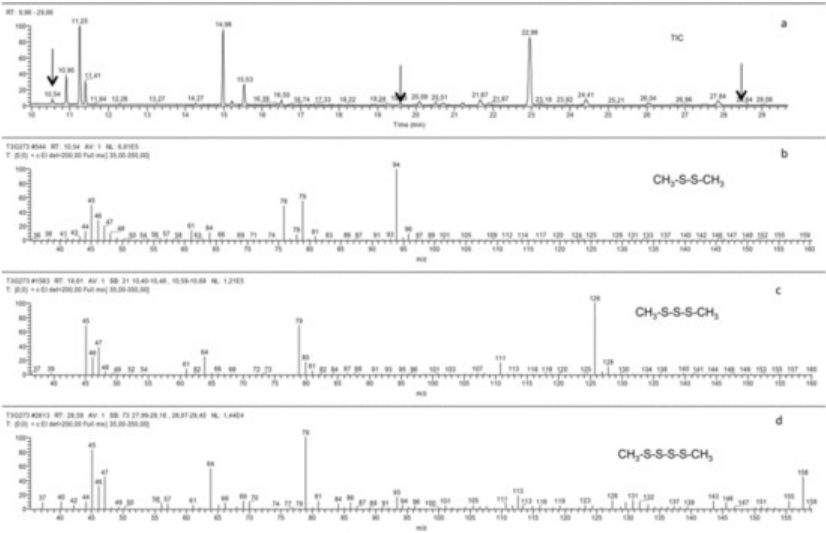


Fig. 1 Total ion chromatogram (TIC) from GC–MS analysis of bottled water with sulphur derivatives (a) and mass spectrum of DMS (b) DTMS (c) and DMTES (d) from compounds detected in the sample M1.

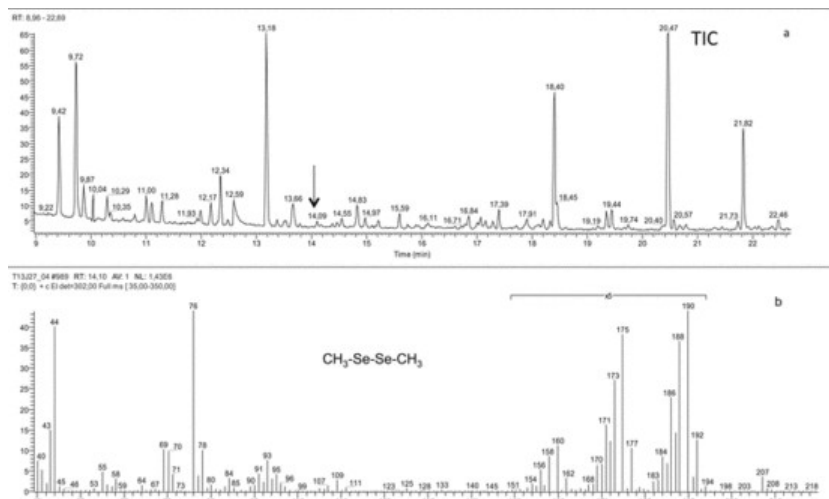


Fig. 2 Total ion chromatogram (TIC) from GC-MS analysis of bottled water with DMDSe (a) and its mass spectrum distribution of Se in amplified (b) from compounds detected in bottled mineral water.

### 3.1.1 Methyl sulphides

The characteristics of the natural biogeochemical sulphur cycle in the atmosphere-biosphere-ocean system are well known (Lovelock et al., 1972). In the +6 oxidation state, the chemistry of sulphur is dominated by sulphuric acid and sulphate that are rather non-volatile chemical species. As only this oxidation state is stable in the presence of oxygen, sulphate is the predominant form of sulphur existing in seawater, fresh water and soils (Andreae, 1990). Therefore, the reduction of sulphate to a more reduced species is a necessary prerequisite for the formation of sulphur volatile compounds. There are two biochemical pathways that lead to sulphate reduction: assimilatory and dissimilatory. Algae in open ocean waters carry out the main transformation, where DMS is the predominant volatile sulphur compound. In addition, other factors can lead to the same results, like other microorganisms as bacteria (Lomans et al., 2001) or under aerobic and waterlogged conditions (Banwart and Bremner, 1976).

The presence of volatile sulphur compounds has been previously detected in water samples from lakes (Hu et al., 2007; Simo et al., 1993), tap water (Wajon and Heitz, 1995; Wajon et al., 1985); ocean water (Davison et al., 1996), wastewater (Hwang et al., 1995), lagoons (Moret et al., 2000) and sea (Simo et al., 1997) and there is one reference in refillable bottles of polyethylene terephthalate (PET) (Widén et al., 2005).

### 3.1.2 Methyl selenides

As in the case of sulphur, selenium can be found in the environment in several oxidation states. The main oxidation states in water are +6 like a selenate ( $\text{SeO}_4^{2-}$ ) and +4 like a selenite ( $\text{SeO}_3^{2-}$ ) (Pyrzynska, 2002; Wake et al., 2004). In natural waters, selenium is present as Se (VI), but the occurrence of Se (IV) is also significant when pH is lower (2.2 in mine drainage) (Bujdoš et al., 2005). These compounds can turn into volatile compounds such as DMSe and DMDSe, where Se has an oxidation state -2. Fungi (Fleming and Alexander, 1972), bacteria (Dungan and Frankenberger, 2001, 2000; Stolz and Oremland, 1999), plants (Flury et al., 1997; Ganther et al., 1966; Zieve and Peterson, 1984), algae (Ansede and Yoch, 2006; Neumann et al., 2003), animals (Ganther et al., 1966) and the combination between acid and UV-light irradiation (Guo et al., 2003) can be considered as the responsible factors for these transformations.

The Se biological cycle is very similar to that of sulphur. However, in contrast to the sulphur, the biogeochemical selenium cycle has not been well defined so far. To explain the Se transformation by microorganisms several mechanisms pathways have been suggested. The first mechanism pathway was suggested by Challenger (Challenger, 1953), but without taking into account the generation of DMDSe. Subsequently, several Se methylation pathways have been suggested (Doran, 1982; Reamer and Zoller, 1980). In general, the formation of methyl selenides from selenate and selenite occurs through several successive reduction and methylation steps.

The presence of volatile selenide compounds has been previously detected in water samples from saline lakes, wastewater and rivers (Cooke and Bruland, 1987) but there are no references from bottled mineral waters.

## 3.2 Quality parameters of the method

The results of linear range, correlation coefficient, IDL, IQL, repeatability, reproducibility and recovery are shown in Table 1. The linearity range shown in Table 1 is enough when dealing with concentrations like the ones obtained in the original samples. Samples M1, M3, M6, M8 and M12 were diluted with previously analysed mineral water so that they fell within the linearity interval. Calibration curves were linear in this range and the values of their correlation coefficient ( $R^2$ ) are above 0.999 for all the analytes. The concentrations of DMDS, DMTS and DMDSe in water bottled can be obtained from their IDL values in pg from Table 1, resulting in 0.036 ng/L, 0.055 ng/L and 0.086 ng/L, respectively. All the IDL values were less than 1 ng/L in original samples. IQL values

are higher than IDL ones, but none of them is higher than 1 ng/L. The results of IQL allow the quantification of the sulphur and selenium derivatives identified in most of the samples.

The relative standard deviations (%RSD), calculated for checking the repeatability with standard concentrations of 1, 2, 7 and 10 ng/L, ranged from 1.2 to 3.9%, this fact pointed out that GC-MS system was performing properly. On the other hand, the %RSD values are lightly higher than repeatability, but all the data were below 10%. Considering that the injection was manual, the values obtained are considered good.

As regard to recoveries, DMTS is by far the compound with the best recovery value (98%) and DMDS value is 50%.The recoveries of these compounds are similar to the ones reported (Gun et al., 2000). DMDSe recovery is low, but having low detection limits provides good detection. The ion base peak has been used to the quantification and the molecular peak has been used to the confirmation, in SIM mode.

### 3.3 Analysis of bottled waters

The volatile-alkylated S and Se species were detected in 23 samples with the objectionable odour described previously. The concentrations of DMDS, DMTS, DMTES and DMDSe have been summarized in Table 2. Regarding the sulphur derivative compounds, the one more frequently detected is DMDS followed by DMTS and finally DMTES has been detected only once. And as can be observed, the concentration of sulphur derivative compounds ranged from 1 to 63 ng/L, among them DMDS has the higher concentration (63 ng/L). On the other hand, DMDSe has been detected eight times, and whose concentration ranged from 4 to 20 ng/L.

Table 2 Concentration (ng/L) of the sulphur and selenium derivatives detected in samples of bottled water.

	CH <sub>3</sub> S <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> S <sub>3</sub> CH <sub>3</sub>	CH <sub>3</sub> S <sub>4</sub> CH <sub>3</sub>	CH <sub>3</sub> Se <sub>2</sub> CH <sub>3</sub>
M1	36	14	8	nd
M2	nd	nd	nd	4
M3	63	2	nd	nd
M4	9	1	nd	8
M5	9.6	1.6	nd	nd
M6	42	nd	nd	nd
M7	15	nd	nd	nd
M8	30	1	nd	nd
M9	nd	nd	nd	5.6
M10	nd	nd	nd	6.4
M11	9	nd	nd	nd
M12	39	nd	nd	nd
M13	0.9	nd	nd	nd
M14	21.6	1.6	nd	nd
M15	3.5	0.7	nd	nd
M16	1.2	d	nd	nd
M17	3.5	1.3	nd	nd
M18	1.2	0.9	nd	nd
M19	4.8	0.8	nd	nd
M20	nd	nd	nd	5.2
M21	nd	nd	nd	14

M22	nd	nd	nd	4
M23	nd	nd	nd	20.2

d: detected nd: not detected.

The sulphur compounds have low odour thresholds (10–25 ng/L for DMDS and 5–10 ng/L for DMTS) (Wajon et al., 1985). The selenium compound has unknown odour thresholds; however, their vapour pressure at 25 °C (0.38 kPa) (Karlson et al., 1994) is well above the 0.01 kPa set in the definition of volatile compounds (WEF-ASCE, 1995). These characteristics favour the detection of these substances by the human nose.

As it can be observed, some of the samples fall below the odour threshold. This can be explained because the water bottles could have been exposed by consumers to higher temperatures than the one in which the odour thresholds were determined. On the other hand, another cause of the problem could have been the water bottles storage from the consumer to the company was not properly conducted. Other study observed some odour changes during the storage at 4 °C, although the changes were not studied further (Wajon et al., 1988). In addition, the simultaneous presence of several compounds derived from sulphur (samples M1, M3, M8, M14, M15, M16, M17, M18 and M19) or sulphur and selenium (M4), could generate a synergistic effect due to the different odours present in the bottle.

The derivative compounds detected are mainly those containing two methyl groups in their molecule. No correlation among derivative compounds from sulphur and selenium has been detected due to the fact that some samples contain only one of them while other samples contain both compounds.

Generally, natural mineral water is chemically and physically stable in spite of slight seasonal fluctuations. The composition of groundwater depends on the type and structure of the rocks which it comes into contact. Nonetheless, in spring and summer, aquifers can have a low level of water where the presence of selenites and sulphates may be higher. The presence of microorganisms in the source water or at some point in the processing and distribution chain, added to the occurrence of selenites and sulphates, may help to generate their methyl compounds.

## 4 Conclusions

- Volatile organic sulphur and selenium compounds have been detected in bottled drinking water having swampy, rotten eggs, sulphidic, cooked vegetable, and/or cabbage odour. Their concentrations range between 1 and 63 ng/L for the sulphur derivatives and between 4 and 20 ng/L for the selenium derivatives.
- The above data allow relating the off-flavour to the compounds studied here. So, they can be considered as good markers when discussing swampy, rotten eggs, sulphidic, cooked vegetable, and/or cabbage odour in water.
- The presence of these compounds in bottled drinking water had never been reported, but under appropriate conditions, the season when water is extracted and the geographical and climatic characteristics can contribute to the presence of sulphur and selenium that can generate some of the derivative compounds studied. Further studies should delve into the study of the water nature before being treated, with the aim of knowing the influence of the aforementioned factors on the water quality.
- CLSA can be considered a good extraction method to isolate these compounds. Despite CLSA requires a long time (2 h) to carry out the extraction, the amount of extract obtained allows doing many analyses using the same extract.
- No synergic effects could be detected between the compounds studied and other volatile compounds identified in the water samples. Owing to the occurrence of sulphur and selenium has been simultaneously detected in only one sample (whose majority compound detected is DMS, followed by DMTS), it can be stated that there is not any direct relationship between the two derivative compounds studied and their occurrence in the water samples.
- There is a need to go in depth into the knowledge of the bottling process, the microbiological quality of water and its geochemistry in order to avoid the presence of substances that are responsible for the off-flavours like the sulphur and selenium compounds here studied.

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